


Production and Characterization of Amorphous Silica Nanoparticles from Coconut Shell and Coir

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Received: 26.07.2021; Revised: 2.09.2021; Accepted: 7.09.2021; Published: 30.10.2021

Abstract: Silica has been produced from coconut coir and coconut shell because of the economic importance of coconut in India. The wastes are generated and disposed of indiscriminately while several are utilized for the energy source. The ash produced by burning them is usually discarded with a considerable amount of extractable silica present. Therefore, extraction of this silica was done using an environmentally friendly chemical approach to produce silica that could be used in several applications. The wastes were calcined at 700°C in a muffle furnace to get ash, treated with HCl to remove soluble metallic oxides, and after that sol-gelled to obtain silica gel. The gel was then dried at 65 °C for 24 hours and characterized using SEM, EDX, FT-IR, and XRD. Silica produced is amorphous with good absorbance potentials. The SEM micrographs show the particles in the Nano size range but with a high level of agglomeration.

Keywords: coconut coir; coconut shell; agricultural wastes; silica; sol-gel.

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1. Introduction

Agricultural wastes have been utilized for the production of several useful materials to reduce their disposal challenges. These wastes are often generated and disposed of indiscriminately or burnt, which results in environmental pollution with adverse effects on climate [1]. The side effects of climate have been a major challenge globally because it leads to the death of about 160,000 people annually, according to the World Health Organization (WHO) [2-5]. India utilized 78% of its landmass, about 2,564,065 square kilometers, to produce several agricultural products and ranked third in eggs, oranges, coconuts, tomatoes, peas, and beans [6]. Literature has shown that agricultural wastes have been used as solid fuel briquettes, adsorbents, cellulose, activated carbon, silica, silicon, refractory, ceramic products, livestock feed, inhibitors, biofuels, construction materials, lignin, and composite reinforcement [7-22]. Silica has been utilized for several applications across industries such as pharmaceuticals, archeology, biomedical, electronics, and silicon feedstock (birth of semiconductor revolution) [23]. It has been used as an intensive blue light emitter, fining agent in the food industry, powder flow agent in the pharmaceutical industry, extra-terrestrial particles collectors, DNA and RNA extractors, and hard abrasives in toothpaste, desiccant, capacitors, and silicon production [24-34].

Silica occurs naturally as quartz with the largest percentage in the earth's crust. It is crystalline in nature with low reactivity. Amorphous silica, on the other hand, finds applications in many areas owing to its advantage of being highly reactive. The non-crystalline type has been synthesized from sodium silicate [35], water glass [36, 37], tetraethoxysilane (TEOS) [38- 40]. It has also been produced from agricultural wastes [19, 34, 41-43, 69, 73] using several methods as reported in reviews [44, 45,]. It is usually prepared by reacting sodium carbonate powder and quartz sand at high temperatures to form sodium silicate, which will then react with sulphuric acid to precipitate silica [46]. The methods used for synthesis from agricultural wastes involve a combination of processes like acid treatment, partial burning (charring), burning, calcination, leaching, enzymatic treatment [47], pyrolysis, hydrolysis, and sol-gel [48, 49].

Among wastes generated in India, coconut wastes stand out because they litter our farmlands, residential and industrial areas because of coconut flesh/juice's economic and social importance. Coconut is a fruit of an Arecaceae plant (palm family) and can be found everywhere across India. India accounts for more than 11 % of the total world production after Indonesia and the Philippines [50]. The fruit is 55 % coir, 15 % shell, and 30 % flesh (meat) and juice [51]. The main part is the meat, where coconut oil and meals are produced. The coir (fibrous part) has been found to be useful for mats, ropes, sacks, door mats, brushes, boat caulks, compost, and fiber for mattresses [50, 52]. Both coir and shell are used as fuels with/without carbon enrichment [50, 53]. With all this utilization, several coir and shells are domestically disposed of indiscriminately. The ash obtained from both contains a huge amount of silica which can be extracted using simple methods [54,].

In this present work, coconut shell and coir have been used to synthesize amorphous silica using calcination and then sol-gel approach.

2. Materials and Methods

2.1. Materials.

Coconut fruits were obtained from Karunya University farm settlement, Karunya Nagar, Coimbatore, India. All reagents used are analytical grades (NICE Chemicals Ltd., Kerala, India).

2.2. Methods.

The procedure used in this work is as highlighted in Figure 1. This procedure involves separating the coir and shell from the main fruit, removing moisture, volatile matter, and carbon to get ash. This is followed by acid treatment to remove soluble oxides of some metals. The sol-gel involves the formation of silicate solution (solation) from ash (see equation 1) and neutralization of the alkaline solution (gelation) to precipitate silica gel ((see equation 2) dispersed in a sodium hydroxide solution. The centrifuge is carried out to separate the silica from the salt solution with washing and to rinse with double distilled water (DDW) to remove NaCl.



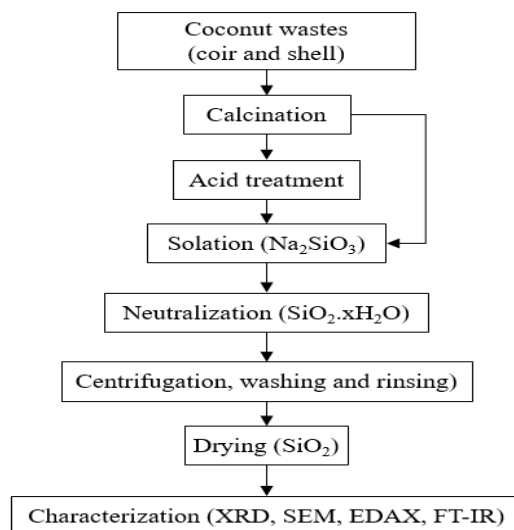


Figure 1. Flow chart of the experimental procedure.

2.2.1. Preparation of coconut coir and shell ashes.

15 pieces of coconut fruits were selected and manually separated into coir, shell, and meat. The coir and shells were sun-dried for 14 days before calcination in a muffle furnace. The samples were put in the furnace and then heated at 6°C/min to 700 oC. The temperature was held for 3 hours and then off with samples left to cool for 12 hours. Afterward, the samples were removed and labeled as coconut coir ash (CCA) and coconut shell ash (CSA) for coir and shell, respectively.

2.2.2. production of silica.

23 g of CCA and CSA were leached with 1.0 M HCl and stirred at 600 rpm for 60 min. Residues were obtained after filtration and rinsing with DDW and then dried in the oven at 105 oC for 24 hours. The dried samples were labeled TCCA and TCSA for CCA and CSA, respectively. For the preparation of sodium silicate from CCA, CSA, TCCA, and TCSA, 12 g of each were added to NaOH at 90 oC for 60 min. 3.0 and 1.0 M of NaOH were used for TCCA and TCSA and 3.0 M for CCA and CSA, respectively. The mixture was allowed to cool and then filtered using Whatman No 1 filter paper. The filtrate was titrated with 1.0 M HCl until the pH of 6.0 to ensure the neutralization of the initial NaOH. This is marked with precipitates of silica gel dispersed in the solution below a pH of 10. This was left to age for 18 hours to get clear supernatant and NaCl solution. The supernatant was decanted, and the remaining silica gel solution was centrifuged at 4000 rpm for 10 mins. The supernatant was decanted, and DDW was added for washing. This step was repeated 3 times. The silica gel obtained was then dried in an oven at 65°C for 24 hours. The silica obtained was then ground for characterization.

2.2.3. Characterization

Silica produced from CCA, CSA, TCCAs and TCSAs were characterized with SEM, EDX, XRD, and FT-IR. SEM was carried out to investigate the morphology and sizes of the silica. EDX was carried out to investigate the chemical composition and invariably the purity of the silica. XRD was to determine the structure of the prepared silica, while FT-IR investigation was carried out to know the functional groups present.

3. Results and Discussion

Figure 2 (a) shows that acid treatment of CCA removed some crystalline phases of metallic oxides marked by disappearance or reduction of crystalline peaks at diffraction angles 27, 41, 50, 58, 63, and 78. This is similar to what is observed in Figure 2 (b) but with some insoluble phases present in treated coconut shell ash. The leaching efficacy of the acid is observed in both coconut coir and shell ashes. This procedure has been reported to be effective for obtaining pure silica [55]. The presence of amorphous silica, which is extractable can, is observed in both the treated and untreated coconut coir and shell ashes. This spread is located between the angle of diffractions 15 and 40° [56,]

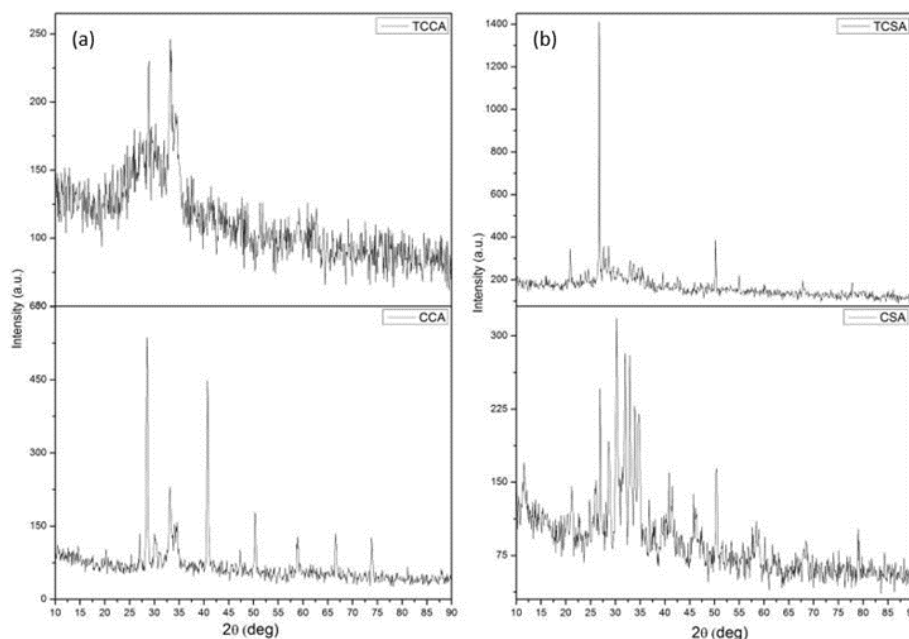


Figure 2. Effect of acid treatment on CCA and CSA.

The amorphous nature of silica produced from both the coir and shell with/without treatments is shown in Figure 3. The crystalline peaks from Figure 3 (a) and Figure 3 (b-UCSA) are unwashed NaCl from the solution. The peaks are found to correspond to JCPDS card nos: 78-0751 and 01-0994. The sodium chloride, as given in equation 2 is due to the neutralization of NaOH reagent used for solution by HCl. This phase can be removed using hot water washing and rinsing that has been reported to be effective for removing any traces of NaCl [56]. Table 1 shows the chemical compositions of silica obtained through the various approaches. The major impurity in the silica obtained is aluminum (as Al₂O₃) which is an amphoteric oxide. This forms precipitates when leached with acid and soluble hydroxide when treated with base. Using a weak base for the solution of CCA yields silica free of aluminum, while it seems difficult for CSA. Hence, the removal of this oxide is a concern. The Na and Cl present can be removed by hot water washing or repeated washing of the silica gel until free of the salt. Figure 4 shows that all the silica produced is below 100 nm. This is due to the method used, which is categorized as an appropriate approach to the synthesis of nanoparticles categorized as a bottom-up approach in the review of Adebisi, Agunsoye [44]. The micrographs also show that there is agglomeration in the procedure used.

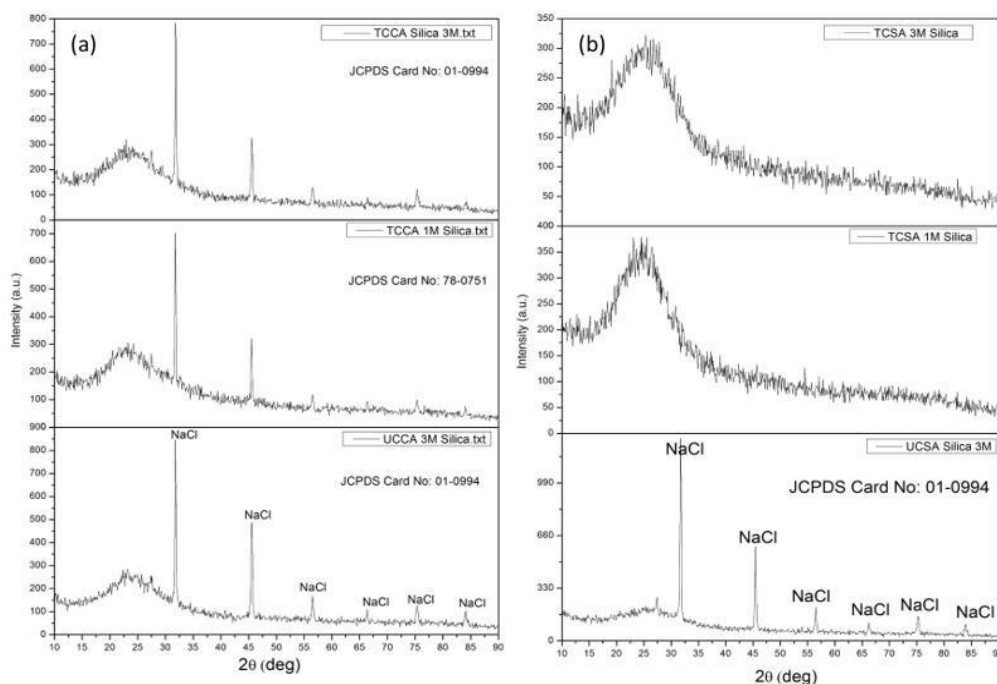


Figure 3. Silica produced from CCA, TCCA, CSA, and TCSA.

Table 1. Chemical composition of silica produced.

Elements	Composition of silica (wt. %)					
	UCCA 3M	TCCA 1M	TCCA 3M	UCSA 3M	TCSA 1M	TCSA 3M
O	54.04	45.3	57.14	56.34	64.49	54.33
Na	4.31	8.76	3.37	4.13		
Al	2.82		2.51	6.12	19.78	5.11
Si	31.33	32.57	32.43	24.62	15.73	40.56
Cl	5.57	11.7	3.46	3.61		
K	1.93	1.67	1.09	5.19		

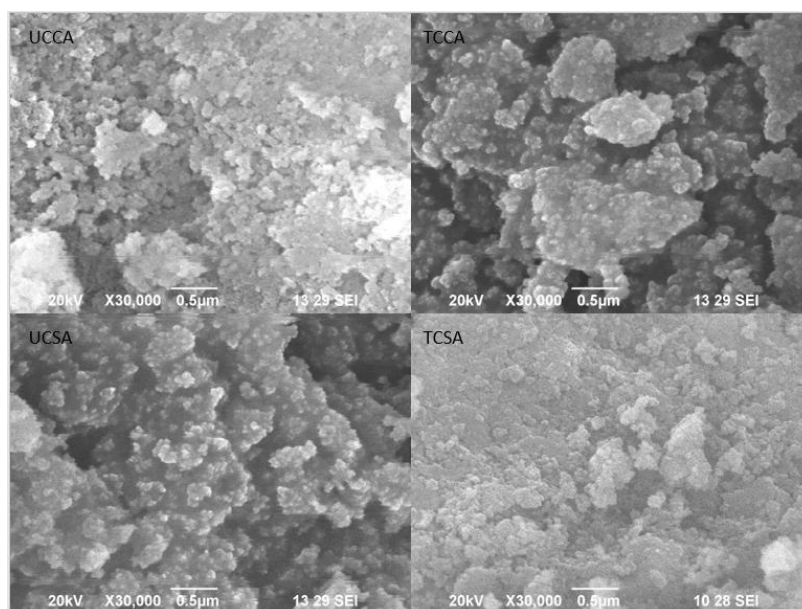


Figure 4. SEM micrographs for untreated and treated coconut coir and shell silica.

The FT-IR spectrum of silica produced from the coir and shell is shown in Figure 5. Silica is characterized by band between 400 and 1300 cm^{-1} [42, 55, 57-66]. The spectra from prepared silica exhibit bands at 448, 796, and 1085 cm^{-1} , corresponding to characteristics rocking of the Si-O bond, bending, and symmetric and asymmetric stretching of the Si-O-Si bond, respectively [42]. Drying the samples at 65 oC left the samples with OH and H-O-H

bonds for silanol and adsorbed water [57]. The band at 1642 cm^{-1} corresponds to H-O-H twisting. The band spreading from 2600 to 3800 cm^{-1} represents stretching vibrations of the surface silanols (Si-OH) groups excited by hydrogen bonds of either water adsorbed or those between Si-O molecules [55, 57,]. The high transmittance values of silica obtained from the untreated samples (CCA and CSA) translate low absorbance compared to those from treated samples. This characteristic high peak of the untreated samples has been reported by Carmona, Oliveira [57, 67-71].

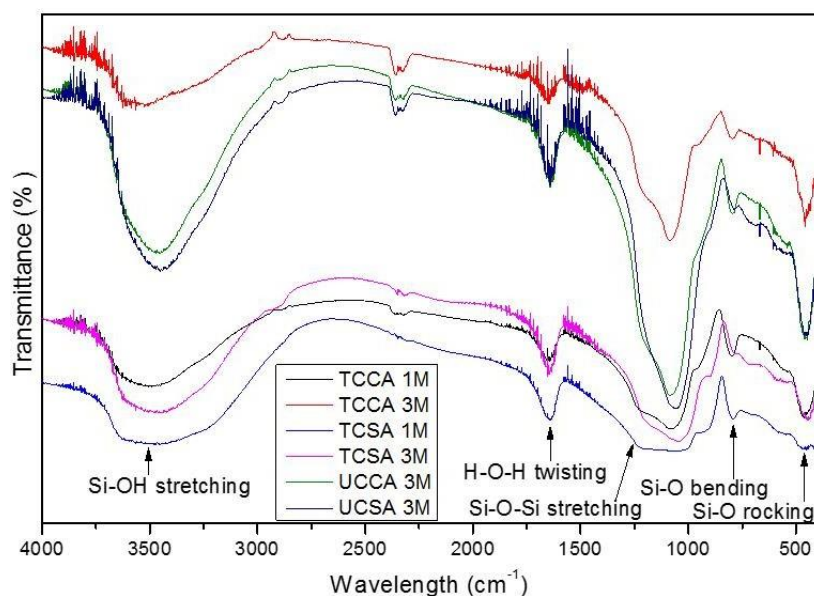


Figure 5. Infrared bands of prepared silica.

4. Conclusions

Silica nanoparticle has been produced from coconut wastes using simple chemical methods. Acid treatment of the ashes is effective for the removal of metallic impurities. It also activates the bonds of both coir and shell samples with good absorbance properties, as inferred from the FT-IR spectrum. Impurities observed in the silica from EDX are Al and K but residual Na and Cl from the titration procedure. The silica particles produced are less than 100 nm but highly agglomerated due to high attraction between the Si-O and Si-OH bonds. XRD results show the silica from both the coir and shell of coconut are amorphous.

Funding

This research received no external funding.

Acknowledgments

The authors acknowledge Karunya University for technical support.

Conflicts of Interest

The authors declare no conflict of interest.

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